

EFFECT OF VARIOUS POLYCRYSTALLINE HYDROCARBON MATRIXES ON THE ELECTRONIC VIBRATIONAL SPECTRA OF FREE BENZYL RADICALS

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There have been made out comparison investigations of electronic vibrational spectra of benzyl free radicals in matrices n-pentane, isooctane and cyclohexane at 4.2 K. The study of luminescence spectra in paraffin hydrocarbon matrices at low temperatures allows rather extensive evidence on fundamental frequencies of radicals especially electron state to be gained.

Keywords: organic compounds, free benzyl radicals, electronic vibrational spectr.

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INTRODUCTION

Extensive information about the electronic vibrational frequencies of some methylbenzenes was obtained using the Shpolsky method.

In this work, comparative studies of the electronic vibrational spectra of free benzyl radicals in n-pentane, isooctane, cyclohexane matrices at 4.2 K were carried out for the first time. The study of luminescence spectra in paraffinic hydrocarbon matrices at low temperatures made it possible rather rich data on the fundamental frequencies of radicals, in the ground electronic state.

It is known that under UV irradiation of methyl-substituted benzene free radicals of benzyl are formed with elimination of one hydrogen atom from CH-group. There are numerous works in the literature on the luminescence spectra of benzyl radical. The study was carried out in a discharge [1, 2], glassy like frozen solutions [3]. The richest information on the electronic vibrational spectra of free benzyl radical was obtained in n-paraffins [4-7] and inert gas matrices[8].

EXPERIMENTAL RESULTS AND DISCUSSION

The luminescence spectra of the benzyl radical shown in the figure (a,b,c) at 4.2 K were obtained using SDL-2 setup with a DKSS-150 lamp excited by a wavelength of 319 nm. Radical samples were obtained by irradiating the initial toluene molecules in hydrocarbon matrix with the solution concentration 10^{-2} - 10^{-3} mol/l.

The vibrational structure in the luminescence spectrum of benzene l in used hydrocarbons (n-pentane, isooctane, cyclohexane) is rather thin in structure and similar to each other. Differences are connected only with a slightly different location of the intensity between the electronic vibrational bands coinciding in frequencies. The lack of multiplicity in the luminescence spectrum of benzene in n-pentane makes is easy to identify electronic vibrational frequencies in this and compare them with the frequencies that appear in other matrices. Comparing

the spectra it is seen that due to the polycrystalline matrix in luminescence spectrum of benzyl radical there have been taken place substantial changes in 0-0 band intensity in a number of n-pentane, isooctane and cyclohexane matrices.

In n-pentane matrix 0-0 band has a very high intensity much higher than the intensity of electronic vibration band for non-totally symmetrical vibration 612 cm^{-1} in frequency. When passing to the isooctane matrix, the intensity of the 0-0 band decreases and becomes almost 2 times less than the bands related to the indicated non-totally symmetrical frequency. Father sharp decrease of the first band intensity takes place in cyclohexane matrix. In this case the intensity of electronic vibration bands complying with the non-totally symmetrical vibration 610 cm^{-1} is essentially similar in isooctane and cyclohexane but it slightly changes in n-pentane.

In Table shows the position of the 0-0 band the main electronic vibrational frequencies measured by us from the luminescence spectrum of benzyl in these three matrices, as well as their comparison with the spectrum argon matrix [8]. Indicated electronic vibrational frequencies and distribution of intensity in luminescence spectrum of benzyl radical in n-pentane identified by us very well match the data of the emission spectrum of these molecules in a neutral argon matrix (see Table), and are also similar to the frequencies in emission spectrum of gas phase (discharge) [1,9]. Such correspondence is probably due to the absence of a significant distorting effect of these matrices on the impurity molecules, which occurs in other polycrystalline matrices - cyclohexane and isooctane.

To illustrate the features of the distortion of the nuclear configuration of benzyl in cyclohexane let's pay attention to the change of electronic vibrational frequencies in the table. Thus, the rather intensive bands corresponding to vibrational frequencies 962 cm^{-1} , 1023 cm^{-1} , 1254 cm^{-1} and 1342 cm^{-1} in pentane disappear in cyclohexane matrix and the bands corresponding to vibrations with the frequencies 523 cm^{-1} and 988 cm^{-1} appear in ~ 2 weakened intensity.

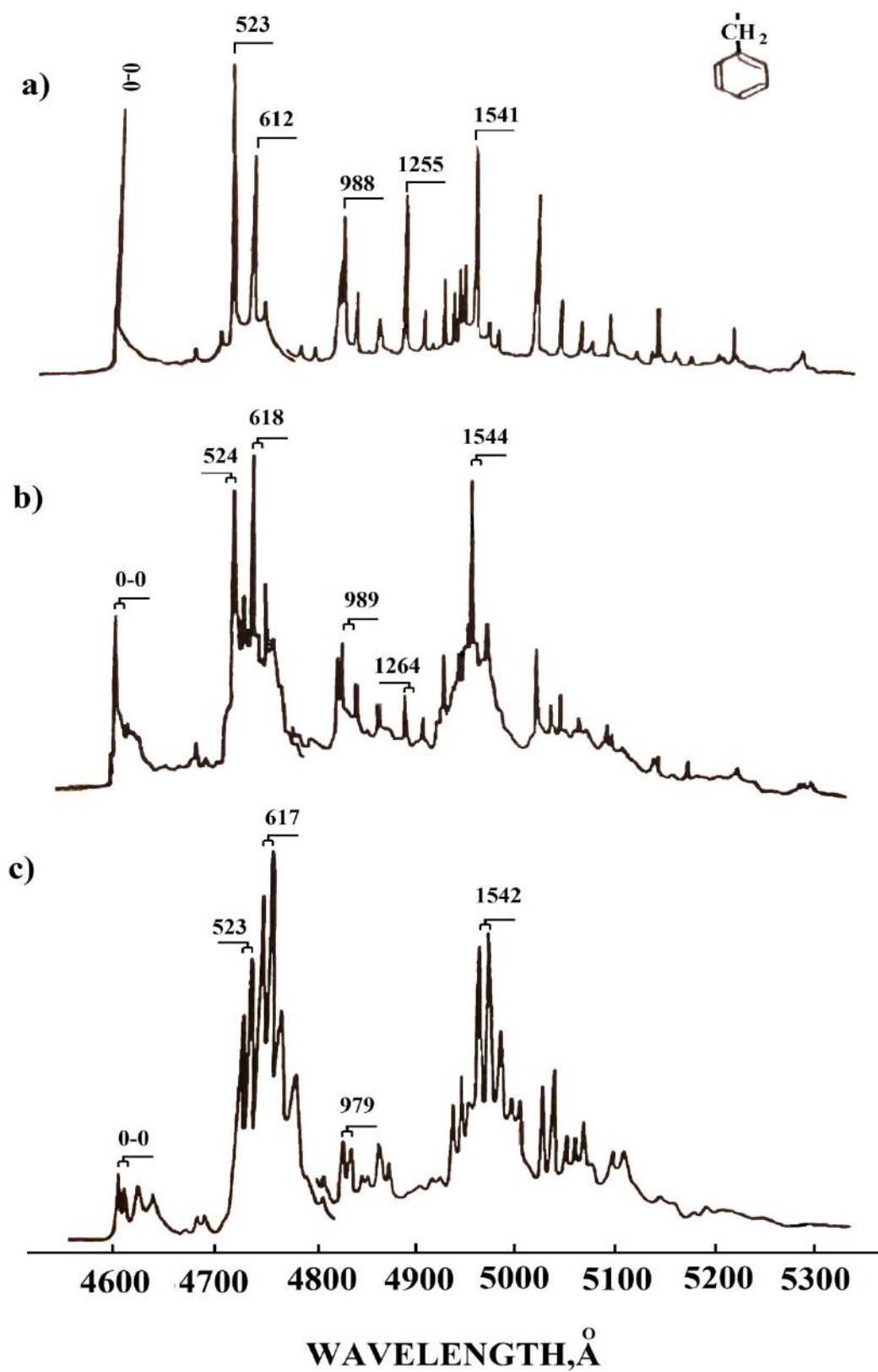


Figure. Luminescence spectra of the benzyl free radicals in various polycrystalline hydrocarbon matrices.

Electronic vibrational frequencies of benzyl radical in fundamental electron state in various matrices

n-Pentan		Isooctane		Cyclohexane		Argon [8]	
ν, cm^{-1}	I	ν, cm^{-1}	I	ν, cm^{-1}	I	ν, cm^{-1}	I
(00)21589	8.4	(00) 21697	4.0	(00)21687	1.2	(00) 21862	4.4
363	0.2	342	0.4	370	0.3	357	0.4
523	8.7	524	8.0	523	5.5	520	8.9
612	5.1	618	8.6	617	8.2	612	10.0
821	0.2	820	0.1	815	0.3		
881	0.2					865	0.2
962	1.4	972	1.0			960	1.1
988	2.2	989	1.2	979	1.1	982	2.2
1023	0.6					1037	0.7
1168	0.1					1085	0.2
1254	2.0	1264	0.8			1255	1.3
1342	0.4	1347	0.4			1335	0.7
1428	0.9	1430	1.0	1436	1.8	1423	2.1
						1462	0.8
						1480	1.3
1541	2.4	1544	3.2	1542	3.4	1530	5.2

Relative intensity of electronic-vibration band ν_{00} -1254 cm^{-1} , and the intensity of ν_{00} band depends on matrix as well. It manifests itself with high intensity in n-pentane, somewhat weakened intensity in isooctane and quite invisible in cyclohexane. The frequency of 1254 cm^{-1} related to the valence vibration of the C-C band also appears in emission spectrum of the benzyl radical in the gas phase (discharge) [1,9]. Change of relative intensity of electronic vibrational band ν_{00} -

1254 cm^{-1} in luminescence spectrum of benzyl radical in different hydrocarbons (n-pentane, isooctane and cyclohexane) is defined by various activity while changing external conditions of valence C-C vibrations.

Thus, rather strong changes in the intensities of the luminescence spectrum 0-0 band of benzyl in the cyclohexane matrix relative to n-pentane due to different molecular symmetry in these mediums.

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**SƏRBƏST BENZİL RADİKALININ ELEKTRON-RƏQSI SPEKTRLƏRİNƏ MÜXTƏLİF
POLİKRIŞTALLİK KARBOHİDROGEN MATRİSALARIN TƏSİRİ**

Benzil radikalının elektron-rəqsi spektrləri n-pentan, izooktan və siklogeksan matrisalarında 4.2 K temperaturunda tədqiq edilmişdir. Alınmış kvazixətti spektrlər benzil radikalının əsas elektron səviyyəsində tezliklərinin kifayət qədər dəqiqliklə təyin edilməsinə imkan verir.

И. Насибов, З. Кадыроглу

**ВЛИЯНИЕ РАЗЛИЧНЫХ ПОЛУКРИСТАЛЛИЧЕСКИХ УГЛЕВОДОРОДНЫХ МАТРИЦ НА
ЭЛЕКТРОННО КОЛЕБАТЕЛЬНЫХ СПЕКТРОВ СВОБОДНЫХ РАДИКАЛОВ БЕНЗИЛА**

Проведены сравнительные исследования электронно-колебательных спектров свободных радикалов бензила в матрицах н-пентане, изооктане в циклогексане при 4.2 К. Изучение спектров люминесценции в матрицах парафиновых углеводородов при низких температурах позволило получение достаточно богатые данные о фундаментальных частотах радикалов, в основном электронном состоянии.